

# Resonance Raman Spectra of Dioxygen Adducts of Pillared Dicobalt Cofacial Diporphyrins

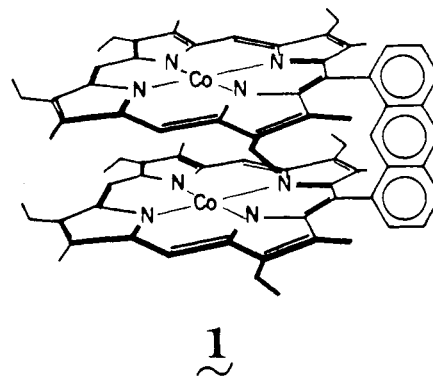
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**Abstract:** The resonance Raman spectra of dioxygen adducts of anthracene pillared cofacial dicobalt(II) diporphyrin (Co-Co complex) have been measured in methylene chloride at  $\sim 190$  K (457.9-nm excitation). In the absence of a base, the Co-Co complex forms a superoxo adduct in which dioxygen is bridged between the two porphyrin planes intramolecularly. This adduct exhibits the  $\nu(\text{O}_2)$  and  $\nu_s(\text{Co-O})$  at 1081 and 628  $\text{cm}^{-1}$ , respectively. Further support of this structure is provided by an ESR spectrum which exhibits a symmetrical 15-peak hyperfine structure. In the presence of a large base such as 4-(dimethylamino)pyridine, the Co-Co complex forms a mixture of the bridging and nonbridging dioxygen adducts in which the base ligands are coordinated to the Co atoms from outside the interporphyrin cavity. The former exhibits the  $\nu(\text{O}_2)$  and  $\nu_s(\text{Co-O})$  at 1098 and 625  $\text{cm}^{-1}$ , respectively, of the bridging adduct whereas the latter shows the  $\nu(\text{O}_2)$  and  $\nu(\text{Co-O}_2)$  at 1139 and 514  $\text{cm}^{-1}$ , respectively, which are typical of nonbridging, six-coordinate dioxygen adducts. Upon raising the temperature, the latter decomposes, and only the former remains at room temperature. If the Co-Co complex solution containing a small base (e.g.,  $\gamma$ -picoline) is oxygenated, only the bands characteristic of nonbridging adducts are observed at 1138 ( $\nu(\text{O}_2)$ ) and 514  $\text{cm}^{-1}$  ( $\nu(\text{Co-O}_2)$ ). On the other hand, the bands characteristic of both bridging and nonbridging dioxygen adducts are observed when the Co-Co complex is oxygenated prior to the addition of the base ligand. These results suggest that a small base can enter inside the interporphyrin cavity, thus blocking the formation of the Co-O-O-Co bridge. Using such spectral patterns as the criteria, we classify 4-phenylpyridine, 4-(dimethylamino)pyridine, 3,5-lutidine, and 3,5-dichloropyridine as "large bases" and pyridine,  $\gamma$ -picoline, 4-ethylpyridine, and 3-ethyl-4-methylpyridine as "small bases". Model building studies show that even "small bases" cannot coordinate to the Co atom from inside the interporphyrin cavity unless the two porphyrin rings are slipped laterally and tilted to take an "open-end" configuration. The subtle difference between 4-(dimethylamino)pyridine (large base) and 4-ethylpyridine (small base) may be explained in terms of steric repulsion between the bifurcated  $\text{N}(\text{CH}_3)_2$  group and the porphyrin plane that exists only in the former.

Dioxygen adducts of binuclear porphyrin complexes are highly important in understanding the reaction mechanisms of cytochrome oxidases<sup>2</sup> and in developing catalysts for electrocatalytic reduction of dioxygen on graphite electrode.<sup>3</sup> In 1977, several groups of workers prepared dimeric porphyrins covalently linked by amido<sup>4,5</sup> or ester<sup>6</sup> bridges in the cofacial configuration. Chang<sup>7</sup> first confirmed the formation of the  $\mu$ -superoxo bridge in the dioxygen adduct of an amido-bridged dicobalt cofacial porphyrin by using ESR spectroscopy. In 1983, Chang and Abdalmuhdi<sup>8</sup> prepared a new type of cofacial diporphyrin in which two porphyrin rings are anchored onto a rigid pillar. The cobalt complexes of these diporphyrins have been shown to be effective electrocatalysts for the 4-electron reduction of dioxygen. While the structures of several metal complexes of diporphyrins have been determined by X-ray<sup>9,10</sup> as well as by ESR,<sup>11</sup> relatively little is known about their dioxygen adducts.

The main objective of this work is to obtain structural information on dioxygen adducts of the Co-Co anthryldiporphyrin (**1**) by using resonance Raman (RR) spectroscopy. During the course of our study, we found a unique feature of this cofacial diporphyrin



(abbreviated as Co-Co complex). For example, a large base such as 4-phenylpyridine and 4-(dimethylamino)pyridine coordinates to the Co-Co complex only from outside the interporphyrin cavity, and oxygenation results in the formation of a Co-O-O-Co bridge inside the cavity. On the other hand, a small base like pyridine and  $\gamma$ -picoline coordinates to the Co-Co complex from inside the cavity, thus preventing the formation of such a bridging dioxygen adduct. The latter does not occur, however, if oxygenation is carried out prior to the addition of the base. Namely, the structure of the dioxygen adduct obtained depends upon the bulkiness of the base ligand and the order of adding dioxygen and the base to the Co-Co complex solution. It was of our particular interest to determine the threshold dimension of the base ligand that can fit into the interporphyrin space.

## Experimental Section

**Compounds.** The Co-Co complex of 1,8-anthryldiporphyrin was prepared by the method reported previously.<sup>8</sup> The bases, pyridine (Py),  $\gamma$ -picoline (pic), 4-(dimethylamino)pyridine (4DMApy), 4-phenylpyridine (4PhPy), 3,5-dichloropyridine (DCP), 3,5-lutidine (Lut), were purchased from Aldrich Chemical Co., while 4-ethylpyridine (4EtPy) and 3-ethyl-4-methylpyridine (3E4MPy) were obtained from Fluka. Pyridine and all liquid pyridine derivatives were vacuum distilled while all solid bases were purified by sublimation prior to use.

(1) (a) Marquette University. (b) On leave from Jagiellonian University, Krakow, Poland. (c) On leave from Technical University, Wroclaw, Poland. (d) Michigan State University.

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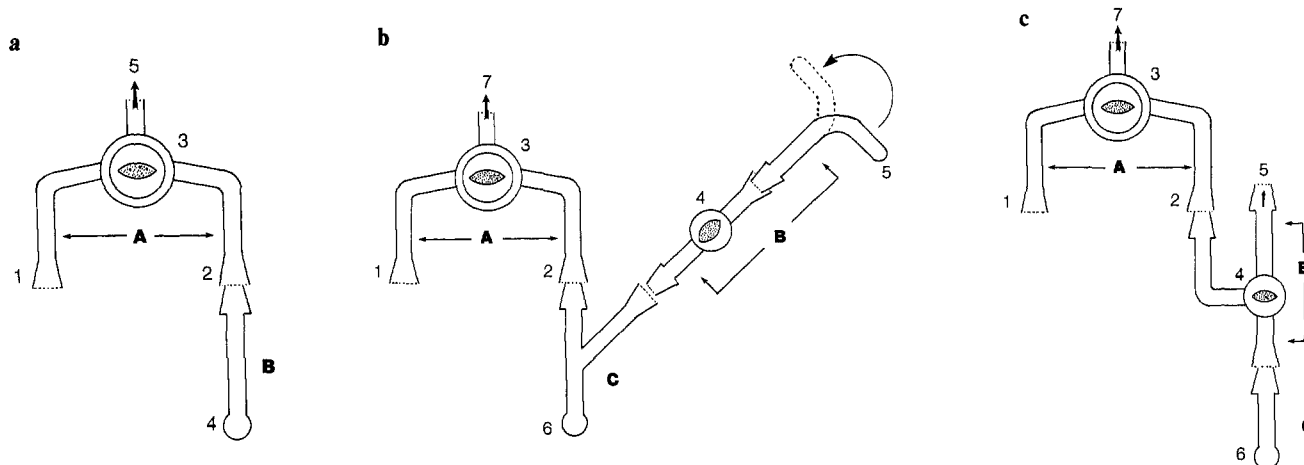


Figure 1. Apparatus used for oxygenation experiments.

The solvents, methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), toluene (tol), and perdeuterated toluene (tol- $d_8$ ), were purchased from Aldrich Chemical Co. Methylene chloride was purified by refluxing for 6 h with calcium hydride,  $\text{CaH}_2$ , and then distilling twice. Toluene was purified by shaking with  $\text{CaH}_2$  for 24 h, refluxing for 4 h, and then distilling twice. The second distillation was over metallic sodium. Perdeuterated toluene was used as received. The gases  $^{16}\text{O}_2$  (prepurified, Matheson) and  $^{18}\text{O}_2$  (98.15% pure, Monsanto Research) were used as received.

As stated in the introduction, it was necessary to prepare the Co-Co complex solution which was oxygenated before or after the addition of the base ligand. For this purpose, we modified our "mini-bulb" technique<sup>12</sup> as described below.

**Method 1: Oxygenation without Base or with Base Added Prior to  $\text{O}_2$  (Figure 1A).** The Co-Co complex ( $\sim 0.7$  mg) was placed into a glass "mini-bulb", labeled 4 in Figure 1A ( $\sim 0.4$  mL in volume) (part B), which was then attached to outlet 2 of a vacuum line (part A) and evacuated. For the reaction involving a crystalline base ligand, the Co-Co complex and 5–10 molar equiv of the base were placed into a "mini-bulb". When a liquid base ligand such as pyridine was employed, a freshly distilled base was transferred to a glass tubing which was attached to inlet 1 of the vacuum line (part A), degassed via 4 freeze-pump-thaw cycles, and transferred under vacuum to the "mini-bulb" containing the Co-Co complex which was immersed in liquid nitrogen. Then the temperature was raised to room temperature and the excess liquid base was vacuum stripped. The glass tubing containing the excess base was removed from inlet 1, and replaced by another glass tubing containing water-free solvent. The solvent was degassed by 4 freeze-pump-thaw cycles and distilled under vacuum to the "mini-bulb" immersed in liquid nitrogen. The temperature of the "mini-bulb" was raised to room temperature to allow the Co-Co complex to dissolve completely in the solvent. Then, the "mini-bulb" was immersed again in liquid nitrogen and oxygen was introduced through inlet 1 to the frozen sample. The pressure of  $\text{O}_2$  was estimated to be around 4 atm at  $-90^\circ\text{C}$  (near the freezing point of the solvent). After oxygen was introduced to the sample, the stem of the "mini-bulb" was sealed at  $\sim 1.5$  cm above the bulb and the sealed "mini-bulb" was attached to a cooled ( $-200^\circ\text{C}$ ) copper cold tip of a CTI Model 21 closed cycle helium cryocooler. This unit permits effective temperature control of the sample. Exact temperature was determined from the relative intensities of the Stokes and anti-Stokes Raman lines of the solvent.

**Method 2: Oxygenation Prior to the Addition of a Liquid Base (Figure 1B).** A freshly distilled liquid base in a glass tubing was attached to inlet 1 of the vacuum line (part A) and after being degassed via 3 or 4 freeze-pump-thaw cycles was distilled into glass adaptor 5 of part B. Next, stopcock 4 was closed, glassware (part B) detached, and the vacuum line (part A) carefully washed to remove traces of the base. About 0.7 mg of the solid Co-Co complex was transferred carefully into a "mini-bulb", labeled 6 (part C). Then, part B was connected to part C which was attached to the vacuum line through outlet 2 and evacuated. A glass tubing with the purified solvent was attached to inlet 1, and the solvent was degassed by 4 freeze-pump-thaw cycles and distilled to the "mini-bulb" immersed in liquid nitrogen. The "mini-bulb" was taken out from the liquid nitrogen and the temperature was raised slowly to room temperature to dissolve the Co-Co complex completely. After the

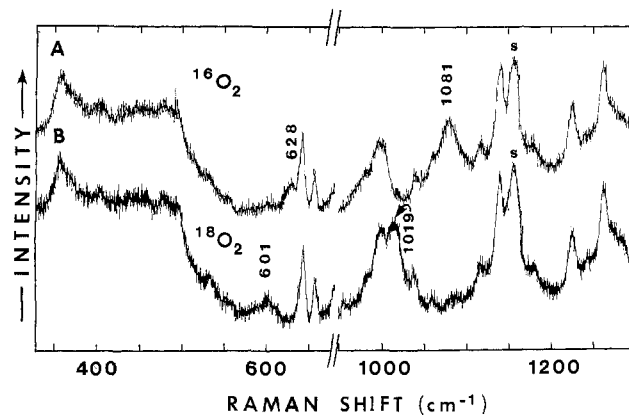


Figure 2. RR spectra of dioxygen adducts of the Co-Co complex in  $\text{CH}_2\text{Cl}_2$  at 190 K (457.9 nm excitation): (A)  $^{16}\text{O}_2$  and (B)  $^{18}\text{O}_2$ .

"mini-bulb" was immersed again in liquid nitrogen, an oxygen line was connected to inlet 1 and oxygen transferred to the frozen sample in the "mini-bulb". Then, the bent glass adaptor 5 (part B) was rotated by  $180^\circ$  and stopcock 4 was opened to allow 1–2 drops of the liquid base to flow down to the "mini-bulb". Following the procedure described in Method 1, the "mini-bulb" was sealed and attached to the cold tip of our cryocooler system.

**Method 3: Oxygenation Prior to the Addition of a Solid Base (Figure 1C).** About 0.7 mg of the Co-Co complex was placed into the glass "mini-bulb", labeled 6 (part C), which then was attached to outlet 2 of a vacuum line (part A) through part B and evacuated. Outlet 5 was closed. A glass tubing with dry solvent was attached to inlet 1, and the solvent was degassed and distilled to the "mini-bulb". The sample was dissolved in the solvent and frozen again in liquid nitrogen as described in Method 1. Then, oxygen was introduced to the sample through inlet 1, and stopcock 4 was opened all 3-ways to allow excess oxygen to escape through outlet 5. Small crystals of a solid base were added to the sample as quickly as possible through outlet 5, stopcock 4 was closed, and the flow of oxygen was stopped. Following the procedure outlined in Method 1, the "mini-bulb" was sealed and attached to the cold tip of the closed cycle helium refrigerator.

**Spectral Measurements.** The RR spectra were measured on a Spex Model 1403 double monochromator connected to a Spex Laboratory Coordinator DM1B. About 12–16 scans were made to obtain the spectra. A Coherent Innova I-100K3 krypton ion laser and a Spectra-Physics Model 2025-05 argon ion laser were used for 406.7 (10 mW) and 457.9 nm (30–35 mW) excitation, respectively. The unperturbed solvent bands were used for frequency calibration. Accuracy of the frequency reading was  $\pm 1$   $\text{cm}^{-1}$  for sharp bands and  $\pm 2$   $\text{cm}^{-1}$  for broad, "noisy" bands.

ESR spectra were measured on a Varian E-4 instrument with  $\text{CH}_2\text{Cl}_2$  as solvent.

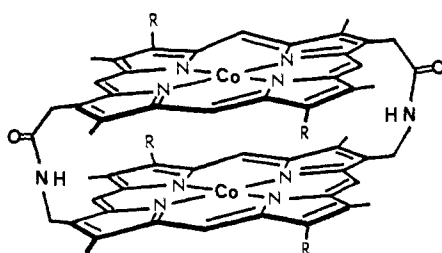
## Results and Discussion

**Oxygenation without Base Ligand.** Figure 2, A and B, shows the RR spectra of methylene chloride solutions of the Co-Co complex which are saturated by  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , respectively, at

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190 K. The band at  $1081\text{ cm}^{-1}$  of the former is shifted to  $1019\text{ cm}^{-1}$  by  $^{16}\text{O}_2/^{18}\text{O}_2$  substitution. Therefore, these bands must be assigned to the  $\nu(\text{O}_2)$  of the respectively dioxygen adducts. The observed isotopic shift ( $62\text{ cm}^{-1}$ ) is very close to that expected for a harmonic diatomic oscillator ( $63\text{ cm}^{-1}$ ). In the low-frequency region, the weak band at  $\sim 628\text{ cm}^{-1}$  is shifted to  $601\text{ cm}^{-1}$  by  $^{16}\text{O}_2/^{18}\text{O}_2$  substitution. In general, the  $\nu(\text{Co}-\text{O}_2)$  of "end-on" type dioxygen adducts of cobalt porphyrins<sup>13</sup> and  $\text{Co}(\text{salen})$ <sup>14</sup> are observed in the  $530\text{--}510\text{ cm}^{-1}$  region. On the other hand, the  $\nu_s(\text{Co}-\text{O})$  of the  $\text{Co}-\text{O}-\text{O}-\text{Co}$  bridges in the  $[(\text{NH}_3)_5\text{Co}(\text{O}_2^-)\text{Co}(\text{NH}_3)_5]^{5+}$  and  $[(\text{NH}_3)_5\text{Co}(\text{O}_2^{2-})\text{Co}(\text{NH}_3)_5]^{4+}$  ions are at  $625\text{--}613$  and  $648\text{--}642\text{ cm}^{-1}$ , respectively.<sup>15</sup> Thus, the observed frequency ( $628\text{ cm}^{-1}$ ) is close to the  $\nu_s(\text{Co}-\text{O})$  of the superoxo-type  $\text{Co}-\text{O}-\text{O}-\text{Co}$  bridge mentioned above.

Six possible modes of  $\text{O}_2$  binding are illustrated in Chart I. According to X-ray analysis on the analogous Ni-Ni complex,<sup>9</sup> the two porphyrin rings are slipped laterally by  $2.40\text{ \AA}$  to minimize van der Waals repulsion between them. The dotted line in the chart indicates the side view of the inclined anthracene ring. Structures I, IA, II, and IIA containing end-on dioxygen can be ruled out since the  $\nu(\text{O}_2)$  of the base-free, five-coordinate Co porphyrin such as  $\text{Co}(\text{TPP})\text{O}_2$  is at  $1278\text{ cm}^{-1}$  in Ar matrices.<sup>16</sup> The IR spectra of co-condensation products of the Co-Co complex with  $\text{O}_2/\text{Ar}$  at  $\sim 15\text{ K}$  also exhibit the  $\nu(^{16}\text{O}_2)$  and  $\nu(^{18}\text{O}_2)$  bands at  $1263$  and  $1192\text{ cm}^{-1}$ , respectively.<sup>17</sup> This leaves only structure III and IV in which the  $\text{O}_2$  is bridged between the two porphyrin planes in a trans conformation. In both structures, the  $\text{O}-\text{O}$  bond is almost parallel to the porphyrin rings. However, a structure such as III would involve unrealistically short and long Co-O bonds due to lateral slippage ( $2.4\text{ \AA}$ ) of the two porphyrin rings mentioned earlier.<sup>9</sup> Recently, Kim et al.<sup>18</sup> carried out X-ray analysis on a dicobalt "face-to-face" porphyrin containing two four-atom amide bridges and found that its interporphyrin distance is only  $3.54\text{ \AA}$  and the two porphyrin rings are stacked almost exactly on top of each other. Based on these structural constraints, they proposed structures III' and III'' of Chart II for its  $\text{O}_2$  adduct. We have measured the RR spectrum of the  $\text{O}_2$  adduct of a similar amide bridged cofacial dicobalt diporphyrin<sup>7</sup> (structure 2). It



DP-4 R= PENTYL



exhibits the  $\nu(\text{O}_2)$  at  $1085\text{ cm}^{-1}$  ( $1026\text{ cm}^{-1}$  for the  $^{18}\text{O}_2$  adduct). We attribute this band to structure III' of Kim et al., since the end-on type coordination of the dioxygen in structure III'' is expected to give the  $\nu(\text{O}_2)$  at a frequency higher than  $1085\text{ cm}^{-1}$ . In this case, structure III' is reasonable since the dioxygen is bonded symmetrically to the Co atoms with reasonable Co-O distances. Evidently, the amide-linked DP-4 cannot form an  $\text{O}_2$  adduct such as IV. In contrast, structure IV is preferred to structure III in the case of the anthryl Co-Co diporphyrin dis-

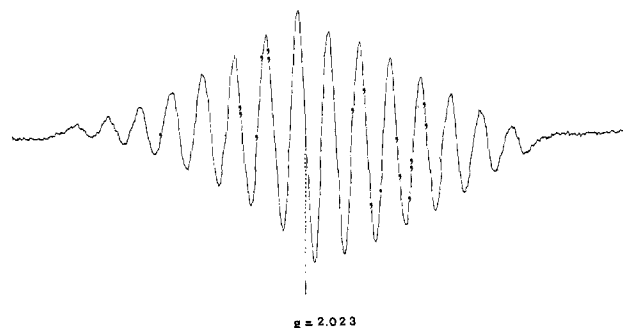


Figure 3. The ESR spectrum of the dioxygen adduct of the Co-Co complex in methylene chloride at room temperature.

Chart I

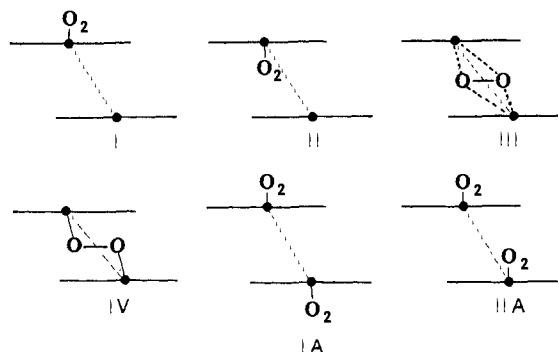
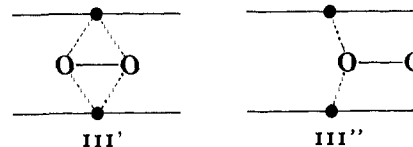


Chart II



cussed above. It is interesting to note that the  $\nu(\text{O}_2)$  of structure III' ( $1085\text{ cm}^{-1}$ ) is similar to that of structure IV ( $1081\text{ cm}^{-1}$ ). This result seems to suggest that the net negative charge on the  $\text{O}_2$  is similar between them since structure III' involves more  $\pi$ - but less  $\sigma$ -bonding than structure IV.

The  $\mu$ -superoxo structure was further substantiated by ESR spectroscopy. The dioxygen adduct of the Co-Co complex obtained in the above manner exhibited a symmetrical 15-peak hyperfine structure due to bonding to the two equivalent  $^{59}\text{Co}$  nuclei ( $I = 7/2$ ), best interpreted as the  $\mu$ -superoxo  $[\text{Co}-\text{O}_2-\text{Co}]^+$  ion. Previously, Le Mest et al.<sup>19</sup> have shown that, even in the absence of base ligands, their dicobalt cofacial porphyrin reacts slowly with  $\text{O}_2$  to form such a  $\mu$ -superoxo complex in  $\text{CH}_2\text{Cl}_2$  at room temperature. In our RR experiments, the bridged complex was formed relatively fast due to high pressure of  $\text{O}_2$  in a mini-bulb ( $\sim 4\text{ atm}$ ). We have alternatively used a different method to prepare the bridged superoxo species by mixing the  $\text{Co}(\text{II})-\text{Co}(\text{II})$  and  $\text{Co}(\text{III})-\text{Co}(\text{III})$  complexes in a 1:1 molar ratio in  $\text{CH}_2\text{Cl}_2$  at room temperature in the presence of air. This solution exhibited the ESR spectrum of the 15-line  $\mu$ -superoxo species shown in Figure 3 and the RR spectrum similar to that shown in Figure 2. Thus, the dioxygen adduct responsible for the  $\nu(\text{O}_2)$  and  $\nu(\text{Co}-\text{O}_2)$  bands of Figure 2 must be attributed to the superoxo  $[\text{Co}-\text{O}_2-\text{Co}]^+$  bridge.

**Oxygenation in the Presence of Large Base Ligand.** First, we consider the case where a large base ligand such as 4-phenylpyridine or 4-(dimethylamino)pyridine (4DMAPy) is added to the solution of the Co-Co complex, and then the resulting solution is reacted with  $\text{O}_2$ . Figure 4, A and B, shows the RR spectra of  $\text{CH}_2\text{Cl}_2$  solutions containing 4DMAPy that were saturated with  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , respectively. These spectra are highly unique in

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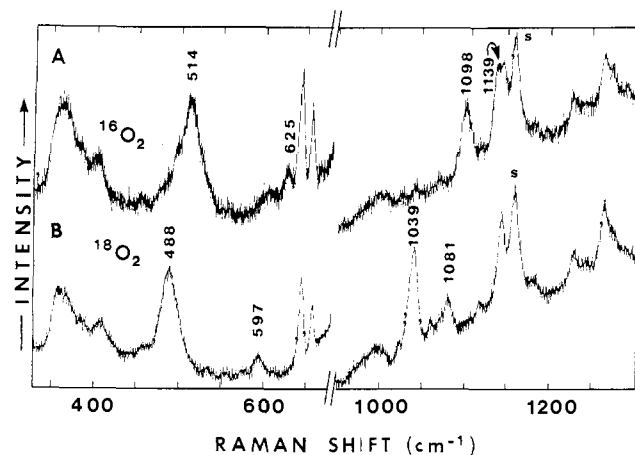


Figure 4. RR spectra of dioxygen adducts of the Co-Co complex in  $\text{CH}_2\text{Cl}_2$  containing 4-(dimethylamino)pyridine at 190 K (457.9 nm excitation): (A)  $^{16}\text{O}_2$  and (B)  $^{18}\text{O}_2$ .

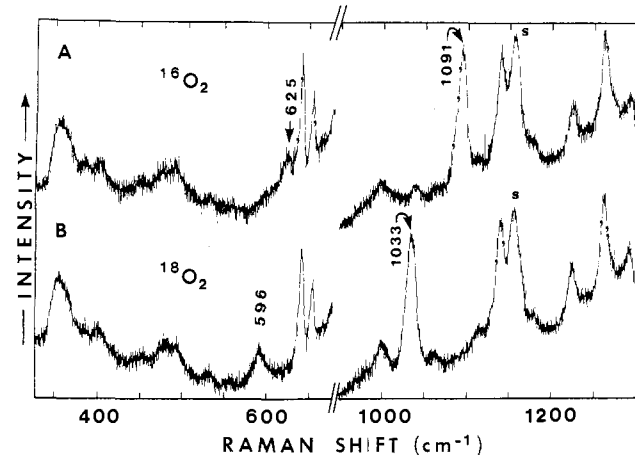


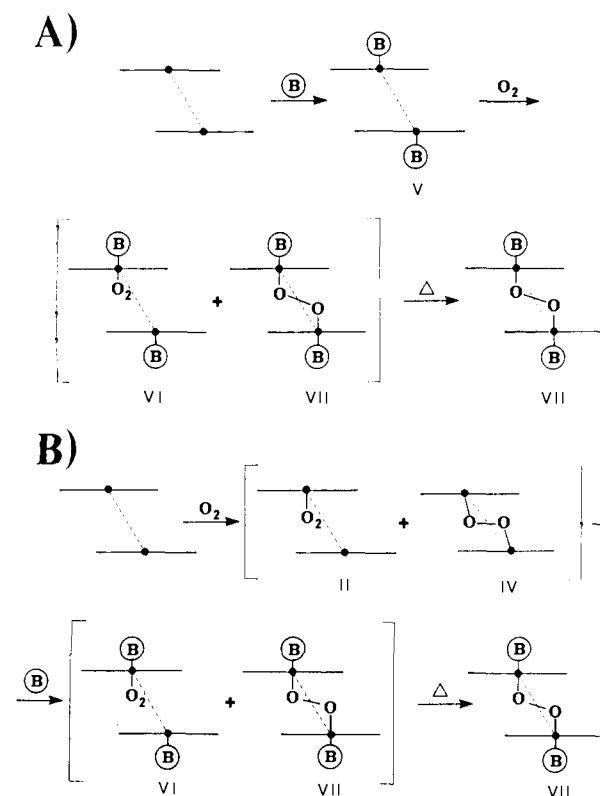
Figure 5. RR spectra of dioxygen adducts of the Co-Co complex in  $\text{CH}_2\text{Cl}_2$  containing 4-(dimethylamino)pyridine at 290 K (457.9 nm excitation): (A)  $^{16}\text{O}_2$  and (B)  $^{18}\text{O}_2$ .

that they exhibit two oxygen-isotope sensitive bands in the 1200–1000- $\text{cm}^{-1}$  region; the  $^{16}\text{O}_2$  solution exhibits the bands at 1139 and 1098  $\text{cm}^{-1}$ , which are shifted to 1081 and 1039  $\text{cm}^{-1}$ , respectively, by  $^{16}\text{O}_2$ - $^{18}\text{O}_2$  substitution. Again, the observed shifts are very close to that expected for a harmonic diatomic oscillator. Although the 1139- $\text{cm}^{-1}$  band is partially overlapped by the porphyrin band at 1143  $\text{cm}^{-1}$ , the corresponding  $\nu(^{18}\text{O}_2)$  band is clearly seen at 1081  $\text{cm}^{-1}$ . The  $^{18}\text{O}_2$  spectrum also indicates that the intensity ratio of the bands at 1081 and 1039  $\text{cm}^{-1}$  is ca. 1:3.6. The same ratio may hold for the pair of bands at 1139 (partially overlapped) and 1098  $\text{cm}^{-1}$ .

In the low-frequency region, the  $^{16}\text{O}_2$  solution exhibits a  $\nu(\text{Co}-\text{O}_2)$  band at 514  $\text{cm}^{-1}$  that is shifted to 488  $\text{cm}^{-1}$  by  $^{16}\text{O}_2$ - $^{18}\text{O}_2$  substitution. The magnitude of this shift (26  $\text{cm}^{-1}$ ) is 5  $\text{cm}^{-1}$  larger than that observed for  $\text{Co}(\text{TPP}-d_8)(\text{py})\text{O}_2$ .<sup>20</sup> As will be shown later, this band is a counterpart of the  $\nu(\text{O}_2)$  observed at 1139  $\text{cm}^{-1}$ . The second oxygen-isotope sensitive bands appear weakly at 625 and 597  $\text{cm}^{-1}$ , respectively, for the  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  solutions and are assigned to the  $\nu_s(\text{Co}-\text{O})$  of the bridging adduct, which exhibits the  $\nu(\text{O}_2)$  at 1098  $\text{cm}^{-1}$  (1039  $\text{cm}^{-1}$  for the  $^{18}\text{O}_2$  adduct).

Upon raising the temperature from 190 K to room temperature, the bands at 1139 (1081) and 514 (488)  $\text{cm}^{-1}$  disappear and the band at 1098 (1039)  $\text{cm}^{-1}$  becomes stronger. (In the above and hereafter, the number in the brackets indicates the frequency of the  $^{18}\text{O}_2$  adduct.) This is shown in Figure 5, A and B. Although the band at 1098 (1039)  $\text{cm}^{-1}$  remains at room temperature, it is shifted by 6–7  $\text{cm}^{-1}$  to lower frequency probably due to slight

Chart III



weakening of the O–O bond at room temperature.

Chart IIIA illustrates the probable route of  $\text{O}_2$  binding in the presence of a large base ligand. Since a base ligand such as 4DMAPy is too large to enter inside the cavity, the addition of 4DMAPy to the Co-Co complex yields structure V in which both base ligands occupy the axial positions outside the cavity. Oxygenation of this solution yields two types of dioxygen adducts: one is stable only at low temperatures and exhibits the  $\nu(\text{O}_2)$  at 1139 (1081) and  $\nu(\text{Co}-\text{O}_2)$  at 514 (488), and the other is stable even at room temperature with the  $\nu(\text{O}_2)$  and  $\nu_s(\text{Co}-\text{O})$  at 1098 (1039) and 625 (597)  $\text{cm}^{-1}$ , respectively. The former  $\text{O}_2$  adduct is represented by structure VI since its frequencies are of typical six-coordinate  $\text{O}_2$  adducts of Co porphyrins,<sup>20</sup> whereas the latter is assigned to structure VII in which the two Co atoms are connected by a superoxo bridge mentioned earlier. A more direct support for the latter structure has already been provided by the highly symmetrical 15-peak ESR signal observed for the Co-Co complex in methylene chloride containing tritylimidazole, which was oxygenated at room temperature.<sup>21</sup> Thus, the nonbridged, unstable  $\text{O}_2$  adduct (VI) is decomposed and only the stable, bridged superoxo complex (VII) remains at room temperature. It should be noted that adducts VII and IV are the first examples of superoxo-type Co–O–O–Co bridges formed between two porphyrin planes for which RR spectra were observed.

Essentially the same spectra as that shown in Figures 4 and 5 are obtained when we first saturate the  $\text{CH}_2\text{Cl}_2$  solution of the Co-Co complex with  $\text{O}_2$  and then add 4DMAPy to the solution. Chart IIIB illustrates the oxygenation steps that yield the same products discussed earlier; adducts VI and VII are in equilibrium at 190 K, and only the latter remains at room temperature. As will be shown later, the two routes shown in Chart III, A and B, give different  $\text{O}_2$  adducts when a small base ligand is employed.

Finally, it is interesting to note that the  $\nu(\text{O}_2)$  of VII (1098  $\text{cm}^{-1}$ ) is higher than that of IV (1081  $\text{cm}^{-1}$ ) although both frequencies originate in superoxo-type Co– $\text{O}_2$ –Co bridges. In non-cofacial Co(II) porphyrins, coordination of a base ligand to the trans

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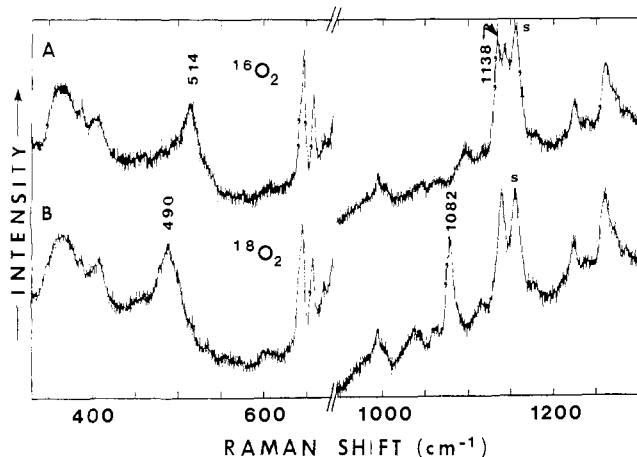
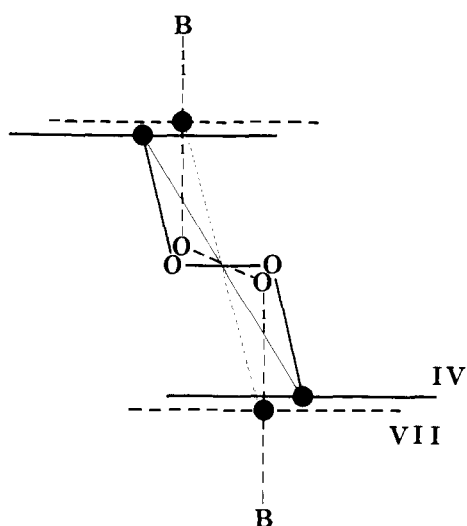


Figure 6. RR spectra of the Co-Co complex in  $\text{CH}_2\text{Cl}_2$  containing  $\gamma$ -picoline to which dioxygen was saturated at 190 K (457.9 nm excitation): (A)  $^{16}\text{O}_2$  and (B)  $^{18}\text{O}_2$ .

Chart IV



position of bound dioxygen lowers the  $\nu(\text{O}_2)$  since the base ligand increases the negative charge on the dioxygen via  $\sigma$  (and  $\pi$ )-donation.<sup>22</sup> In the cofacial Co(II) porphyrin, this trend is reversed as seen above. We suggest that this may be attributed to the unusual structural constraint imposed on the dioxygen connecting the two Co atoms in the cofacial porphyrin. When the base ligand coordinates to the Co atom from outside the cavity, the Co-O bonds tend to take the vertical direction as shown by structure VII. This would bring the Co atoms closer via lateral slippage of the porphyrin planes and shorten the O-O bond relative to that of IV as shown in Chart IV. Apparently, the effect of such structural change on the dioxygen and its  $\nu(\text{O}_2)$  is much greater than that of electron donation to the dioxygen by the base ligand. As stated earlier, the amide-bridged "face-to-face" diporphyrin exhibits the  $\nu(\text{O}_2)$  at 1085  $\text{cm}^{-1}$  in the absence of a base ligand. Upon addition of a base ligand (4DMApy), this band is shifted 5  $\text{cm}^{-1}$  to higher frequency. In this case, the lateral slippage mentioned above may not occur. Thus, the small shift on the  $\nu(\text{O}_2)$  seems to suggest that the symmetrical sandwich structure (III') is less sensitive to the trans-ligand effect due to its unusual coordination geometry.

**Oxygenation in the Presence of Small Base Ligands.** Figure 6, A and B, shows the RR spectra of  $\text{CH}_2\text{Cl}_2$  solutions of the Co-Co complex containing a small base,  $\gamma$ -picoline (pic), that are saturated with  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , respectively, at 190 K. The bands at 1098 (1039) and 625 (597)  $\text{cm}^{-1}$  shown in Figure 4, A and B, are conspicuously missing in these spectra. Thus, small

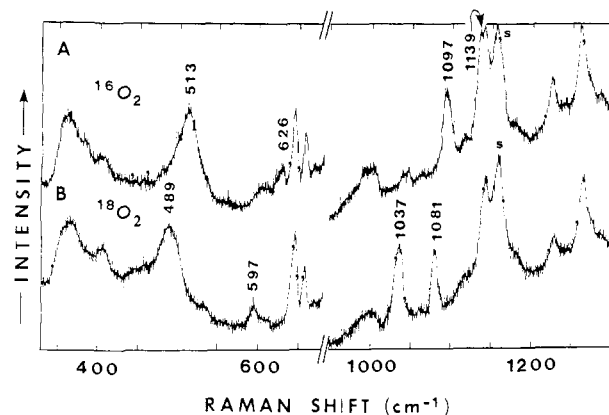
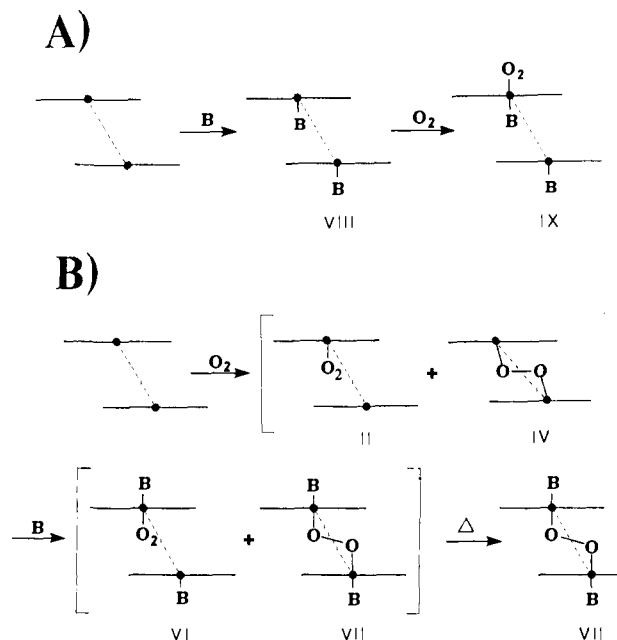


Figure 7. RR spectra of  $\text{CH}_2\text{Cl}_2$  solutions of the Co-Co complex to which dioxygen was added first and  $\gamma$ -picoline was added later (190 K, 457.9 nm excitation): (A)  $^{16}\text{O}_2$  and (B)  $^{18}\text{O}_2$ .

Chart V



base ligands such as pic produce only one type of  $\text{O}_2$  adduct, which exhibits the  $\nu(\text{O}_2)$  and  $\nu(\text{Co-O}_2)$  at 1138 (1082) and 514 (490)  $\text{cm}^{-1}$ , respectively.

The unique feature of the small base ligand is its ability to coordinate to the Co atom from inside the cavity as shown in structure VIII of Chart VA. This structure yields the  $\text{O}_2$  adduct IX which exhibits the  $\nu(\text{O}_2)$  and  $\nu(\text{Co-O}_2)$  at 1138 (1082) and 514 (490)  $\text{cm}^{-1}$ , respectively. Upon raising the temperature, adduct IX is decomposed as evidenced by the disappearance of these bands. If the pic were coordinated outside the cavity (structure V), a mixture of VI and VII would have been formed by oxygenation, and the  $\nu(\text{O}_2)$  of the latter would have been observed near 1098  $\text{cm}^{-1}$  at room temperature. This was not the case.

It is interesting to note that the results are entirely different when  $\text{O}_2$  is added first. Figure 7, A and B, shows the RR spectra of the solutions that were oxygenated prior to the addition of pic at 190 K. These solutions exhibit two  $\nu(\text{O}_2)$  at 1139 (1081) and 1097 (1037)  $\text{cm}^{-1}$  and the  $\nu(\text{Co-O}_2)$  and  $\nu_s(\text{Co-O})$  at 513 (489) and 626 (597)  $\text{cm}^{-1}$ , respectively, which are essentially the same as that shown in Figure 4. Chart VB shows the process of this oxygenation. Thus, when  $\text{O}_2$  is added first, the  $\text{O}_2$  adducts, VI and VII, are formed irrespective of the size of the base ligand, and only the latter remains at room temperature.

As expected, the dioxygen adducts IX and VI shown in Chart V exhibit similar  $\nu(\text{O}_2)$  and  $\nu(\text{Co-O}_2)$  frequencies. Yet we were

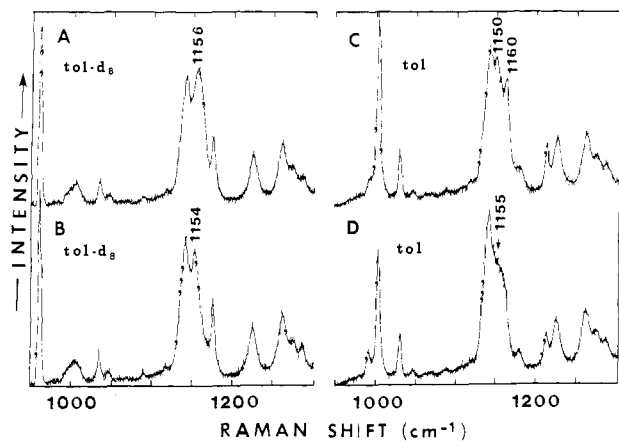


Figure 8. RR spectra of the Co-Co complex in toluene- $d_8$  (traces A and B) and toluene (traces C and D). In traces A and C, pic was added prior to oxygenation. In traces B and D, oxygenation was made prior to the addition of pic. All by 406.7-nm excitation at 190 K.

able to assign the outside- and inside-binding structures to these bands. To provide further support for our assignments, we measured the RR spectra of the Co-Co complex in toluene and toluene- $d_8$  by adding pic before the oxygenation (Figure 8, A and C) and after the oxygenation (Figure 8, B and D). In the former case, the  $\nu(\text{O}_2)$  is observed at  $1156 \text{ cm}^{-1}$  in toluene- $d_8$  (Figure 8A). The bands at  $1174$  and  $1142 \text{ cm}^{-1}$  are due to toluene- $d_8$  and the porphyrin, respectively. Upon changing the solvent to toluene, the band at  $1156 \text{ cm}^{-1}$  (Figure 8A) splits into two bands at  $1160$  and  $1150 \text{ cm}^{-1}$  (Figure 8C). As stated in our previous paper,<sup>23</sup> this splitting occurs when the  $\nu(\text{O}_2)$  is close to the internal mode of toluene ( $1155 \text{ cm}^{-1}$  in this case) and when the bound dioxygen is directly associated with the toluene molecule. Thus, the spectrum shown in Figure 8C strongly suggests the outside binding of dioxygen (structure IX). As shown in Figure 8D, such splitting is not observed when oxygenation is carried out before the base is added; it exhibits only a shoulder band centered at  $1155 \text{ cm}^{-1}$ . This result supports structure VI because steric repulsion from the cofacial porphyrin structure would prevent the approach of toluene to the bound dioxygen.

**Size of Base Ligand and Structure of Dioxygen Adduct.** The results presented above show that when the base ligand is added prior to oxygenation, a large base such as 4DMAPy produces two dioxygen adducts, VI ( $1139, 514 \text{ cm}^{-1}$ ) and VII ( $1098, 625 \text{ cm}^{-1}$ ), whereas a small base such as pic yields only one dioxygen adduct, IX ( $1138, 514 \text{ cm}^{-1}$ ). Here, the numbers in parentheses indicate

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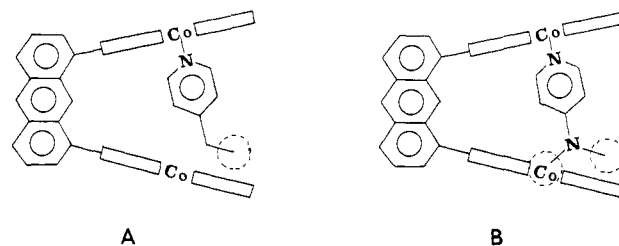


Figure 9. Schematic drawings to show probable orientations of 4-ethylpyridine (A) and 4-(dimethylamino)pyridine (B) in the Co-Co complex.

the  $\nu(\text{O}_2)$  and  $\nu(\text{Co-O}_2)$  or  $\nu_s(\text{Co-O})$  of each  $^{16}\text{O}_2$  adduct. Apparently, these differences originate in the ability or inability of a base ligand to enter the interporphyrin cavity, which is determined by the size and shape of the base ligand. It is, therefore, of great interest to find the threshold dimension of the base ligand by using RR spectroscopy; two  $\nu(\text{O}_2)$  are observed near  $1139$  and  $1098 \text{ cm}^{-1}$  if the base is too large to enter the cavity, and only one  $\nu(\text{O}_2)$  is observed near  $1138 \text{ cm}^{-1}$  if the base is small enough to enter the cavity.

Using such criteria, we found tritylimidazole, 4-phenylpyridine, 4-(dimethylamino)pyridine, 3,5-lutidine, and 3,5-dichloropyridine as large bases. On the other hand, pyridine,  $\gamma$ -picoline, 4-ethylpyridine, and 3-ethyl-4-methylpyridine were found to be small bases. As stated earlier, X-ray analysis on the Ni-Ni complex<sup>9</sup> shows that the two porphyrin rings are slipped laterally by  $2.4 \text{ \AA}$  with respect to each other, giving the Ni-Ni distance of  $4.566 \text{ \AA}$ . If a molecular model of the Co-Co complex is built with this geometry, we readily find that large bases such as tritylimidazole and 4-phenylpyridine cannot coordinate to the Co atom from inside the interporphyrin cavity. The remaining bases can take such coordination geometry if the two porphyrin rings are slipped laterally and further tilted to each other as shown in Figure 9. However, the difference between 4-(dimethylamino)pyridine (Figure 9B) and 4-ethylpyridine (Figure 9A) is subtle. Apparently, the former behaves as a large base because its bifurcated methyl groups on the amino nitrogen atom cause steric repulsion against the porphyrin plane. The difference between 3,5-lutidine (large base) and 3-ethyl-4-methylpyridine (small base) can be explained in a similar manner.

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